International Journal of Advanced Scientific Research
www.allscientificjournal.com
ISSN: 2456-0421
Received: 31-12-2024, Accepted: 30-01-2025, Published: 14-02-2025
Volume 10, Issue 1, 2025, Page No. 10-11

Stability constant of Lanthanum(III), Neodymium(III) and Praseodymium(III) chelates with substituted Schiff's bases

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Abstract

The interactions of La (III), Nd (III) and Pr (III) with 2-hydroxy-5-chloro-1-(a-phenylimino) ethyl benzene (Ligand-L_1), 2-hydroxy-5-chloro-1-(a-para methylphenylimino) ethyl benzene (Ligand-L_2) and 2-hydroxy-3-bromo-5-chloro-1-(a-phenylimino) ethyl benzene (Ligand-L3) have been investigated by pH-metric technique at 0.1 M ionic strength at 26 ± 0.1°C in 70% DMF-water mixture. The data obtained were used to estimate the values of proton-ligand stability constants (pK) and metal-ligand stability constants (log K). It is observed that La (III), Nd (III) and Pr (III) metal ions formed 1:1 and 1:2 complex with all the three ligands.

Keywords: Chelates, La (III), Nd (III), Pr (III), metal – ligands constants pH – ranges

Introduction

The substituted Schiff's bases are good chelating agents as they bear -OH group in the vicinity of >C=N group. The study of their metal complexes is very interesting because of their unusual stability, chemical, electrical and magnetic properties. Metal-ligand stability constants of some lanthanides with some substituted sulphonic acids have also been investigated [1]. The stability constants of Pr (III), Nd (III), Sm (III), Eu (III), Tb (III) metal ion complexes with some substituted isoxazolines have been reported. The stability constants of Pr (III), Nd (III) and Sm (III) chelates with some substituted pyrazolines have also been reported [3]:

Materials and methods

Substituted Schiff's bases were synthesised in laboratory and their purity was checked by I.R., N.M.R. and m.p. The solutions of ligands were prepared in DMF- water (70% v/v) solvent. Dimethyl formamide (DMF) was dried over calcium sulphate for 72 hours followed by distillation under reduced pressure. The solvent thus obtained is used for the experimental purpose.

$HCIO_4$ and NaOH were used of AR-grade. Metal nitrates were dissolved in perchloric acid and their concentrations were estimated by standard methods [4]. The other solutions were prepared in double distilled water pH measurements were carried out with ELICO-LI-10 pH- meter (accuracy ± 0.05 unit) using glass electrode and calomel electrodes at 26 ± 0.1°C. pH- meter was calibrated by standard buffer solution of pH 4.00, 7.00 and 9.20 pH. The ß-values (pH-meter reading in 70% DMF-water mixture) were converted to [H] values by applying the corrections proposed [5].

The overall 0.1 M ionic strength of solution was calculated by the expression:

$$u = \frac{1}{2} + \sum_{i=1} CiZi^2$$

The contribution of the other ions in addition to Nat and CIO, were also taken into consideration.

Experimental procedure involves following three sets of experiments.

1. Free Acid $HCIO_4$ $(1 \times 10^{-2} M)$
2. Free Acid $HClO_4$ $(1 \times 10^{-2} M)$ + substituted ligand solution $(1 \times 10^{-2} M)$
3. Free Acid $HCIO_4$ $(1 \times 10^{-2} M)$ + substituted ligand solution $(20 \times 10^{-4} M)$ Metalions $(4 \times 10^{-2} M)$

Three sets were separately against standard solution of 0.2 M NaOH and 0.1 M ionic strength was maintained constant by adding an appropriate amount of 1 M NaCIO, solution. All the titrations were carried out in 70% DMF-water mixture.

Results and discussion

Proton-Ligand Stability Constants: Substituted Schiff's bases may be considered as monobasic acids having only one dissociable H^+ ion from -OH group. It can therefore be represented as HL.

$$HL \leftrightharpoons H^+ + L^-$$

The titration data were used to construct the curves between volume of NaOH as pH the proton ligand formation numbers (n_{A}) were calculated by Irving and Rossotti's expression [6]. PK values were calculated from formation curves between pH vs n_{A} by noting the pH at which n_{A} = 0.5 (half integral method).

It could be observed from Table-I, that pK values increase in the following order.

Ligand (L_1) > I Ligand (L_2) > Ligand (L_3)

Metal-Ligand Stability Constant: The stepwise formation constants of La (III) Nd (III) and Pr (III) with ligand (L_1) ligand (L_2) and ligand in 70% DMF-water mixture were (L_3) determined. The values of log(K) 1 and log(K) 2 were directly computed from the formation curves (n vs pL) using half method as shown in Table-2.

The deviation between acid curve and (Acid + Ligand) curve showed the dissociation of-OH group from ligand. The departure between (Acid + Ligand) curve and (Acid +

Ligand + Metal) curve showed the commencement of formation of complex. The colour of complexes was observed in the pH range from 5 to 10 shows the formation of complex. The values of - (log(K) 12 -log K 2) and log(K) 1 /log K 2 are presented in Table-3. It could be observed from there is a difference in log K_1 and log tilde K_2 values that showed the stepwise formation of complexes. The smaller difference may be due to trans-structure.

Table 1: Proton-ligand stability constants of substituted schiff's bases in 70% DMF – water mixture

Sr. No.	System	Constant by half integral method
1.	2-Hydroxy-5-chloro-l-($\alpha - phenyl\ imino$) ethyl benzene .... Ligand (L_2)	6.975
2.	2-Hydroxy-5-I-($-\alpha - para\ methyl\ phenyl\ imino$) ethyl benzene .... Ligand (L_2)	5.530
3.	2-Hydroxy-3-bromo-5-1-($\alpha - phenyl\ imino$) benzene .... Ligand (L_3)	4.210

Table 2: Metal- ligand stability constants of La (III), Nd (III) and Pr (III) complexes with substituted Schiff's bases at 0.1 M ionic strength

Sr. No.	System	Constant	
		log K_1 i.e. pL_1	log K_2 i.e. pL_2
1.	La (III) – Ligand (L_1)	5.0099	4.3289
2.	Nd (III) – Ligand (L_1)	5.0198	4.5789
3.	Pr (III) – Ligand (L_1)	4.8297	4.1890
4.	La (III) – Ligand (L_1)	3.4748	3.0347
5.	Nd (III) – Ligand (L_1)	3.9248	3.5839
6.	Pr (III) – Ligand (L_1)	4.0848	3.9463
7.	La (III) – Ligand (L_1)	3.3780	3.3433
8.	Nd (III) – Ligand (L_1)	3.0139	2.9618
9.	Pr (III) – Ligand (L_1)	2.8541	2.6682

The results show that the ratio log K_1 / log K_2 is +ve in all cases. This implies that there is little or no steric hindrance to the addition of secondary molecules.

It could be seen from Table-I that pK value of ligand (L_1) is greater as compared to ligand (L_2) and ligand (L_3). It showed that, the dissociation of -OH group is at a low extent of ligand (L_1).

Validity of log K = a pK + b relation: Many workers have investigated linear relationship between pK and log K [7, 8, 9].

The order of stability of complex is as follows

1. log K_1 for ligand (L_1)
   Nd (III) > La (III) > Pr (III)
2. log K_1 for ligand (L_2)
   Pr (III) > Nd (III) > La (III)
3. log K_1 for ligand (L_3)
   La (III) > Nd (III) > Pr (III)

Table 3: Metal-ligand stability constant at 0.1 M ionic strength

Sr. No.	System	Constant	
		log K_1 –log K_2	log K_1/log K_2
1.	La (III) – Ligand (L_1)	0.6810	1.1573
2.	Nd (III) – Ligand (L_1)	0.4409	1.0963
3.	Pr (III) – Ligand (L_1)	0.4401	1.1529
4.	La (III) – Ligand (L_1)	0.3409	1.1450
5.	Nd (III) – Ligand (L_1)	0.1385	1.0951
6.	Pr (III) – Ligand (L_1)	0.0347	1.0351
7.	La (III) – Ligand (L_1)	0.0521	1.0104
8.	Nd (III) – Ligand (L_1)	3.0139	2.9618
9.	Pr (III) – Ligand (L_1)	2.8541	2.6682

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